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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Preparation of 1,2-Diacyl-2-(t-Alkyl)Hydrazines

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(71) Same as inventor

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Notice: This application is as filed and may therefore contain an incomplete specification.



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ABSTRACT

This invention relates to a process for preparing 1,2-diacyl-2-(*t*-alkyl)hydrazines. More particularly, this invention relates to a process for preparing the aforesaid diacylhydrazine whereby an ester or a mixture of an ester and water is
5 employed as the solvent in a process wherein an aromatic acid chloride is reacted in a first step with a *t*-alkylhydrazine or a corresponding acid addition salt of a *t*-alkylhydrazine such as the hydrochloride salt or the like in the presence of a base to afford a 1-acyl-2-*t*-alkylhydrazine followed by a second step wherein another aromatic
10 acid chloride is reacted with the aforesaid monoacylhydrazine in the presence of a base to afford the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine. Such compounds are known to have excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

The invention also relates to certain 1,2-diacyl-2-(*t*-alkyl)hydrazines which
15 are prepared in accordance with the process of this invention.

PREPARATION OF 1,2-DIACYL-2-(*t*-ALKYL)HYDRAZINESBACKGROUND OF THE INVENTION

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This invention relates to a process for preparing 1,2-diacyl-2-(*t*-alkyl)hydrazines. More particularly, this invention relates to a process for preparing the aforesaid diacylhydrazine whereby an ester or a mixture of an ester and water is employed as the solvent in a process wherein an aromatic acid chloride is reacted in a first step with a *t*-alkylhydrazine or a corresponding acid addition salt of a *t*-alkylhydrazine such as the hydrochloride salt or the like in the presence of a base to afford a 1-acyl-2-*t*-alkylhydrazine followed by a second step wherein another aromatic acid chloride is reacted with the aforesaid monoacylhydrazine in the presence of a base to afford the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine. Such compounds are known to have excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

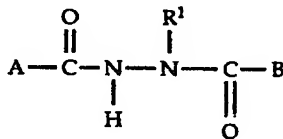
The search for process solvents which are environmentally friendly, which are easily removed from the desired product, which provide good selectivity to the desired intermediates and products, which are easily recovered from the desired products, which allow a facile purification of the desired products, which possess favorable solubility properties for both the reactants and the desired intermediates and products, which can be used in all steps of the process, which are inert to the reaction conditions and which possess favorable process economics is a continuing one because of the difficulty in finding solvents or mixtures of solvents which fulfill all these important conditions. For example, US 4,985,461 discloses a process leading to 1,2-diacyl-2-(*t*-alkyl)hydrazines which employs one or more solvents such as water, alcohols such as methanol, ethanol, isopropanol and the like, hydrocarbons such as toluene, xylene, hexane, heptane and the like, glyme, tetrahydrofuran, acetonitrile, pyridine, haloalkanes such as methylene chloride or mixtures of these solvents. However, all these solvents suffer from one or more of the deficiencies previously noted. For instance, water by itself results in poor intermediate and product yields and selectivity with a large amount of diacylation of the *t*-butylhydrazine occurring in the first process step. Alcohols such as methanol, ethanol, isopropanol and the like react with the acid chlorides, thus resulting in undesirable consumption of the acid chlorides and complicating the recovery and recycle of the process solvents. Hydrocarbons such as toluene, xylene, hexane, heptane and the like provide poor reaction selectivity in the first process step with resultant unacceptable levels of the wrong acylation isomer;

additionally, these solvents are carefully regulated by governmental authorities because of environmental and safety concerns. Glyme and tetrahydrofuran are both ethers which can form undesirable levels of dangerous peroxides upon continued recovery and recycle to the process; they are also quite water soluble which further increases the difficulty of their recovery. Acetonitrile and pyridine not only are both very water soluble and hence difficult to recover in an aqueous system, but also both possess toxicological and safety concerns. Haloalkanes such as methylene chloride have a high vapor pressure which results in difficulty to contain and prevent emissions to the environment; the solubility of usual monoacylhydrazine intermediates and diacylhydrazine products is also usually very high in such solvents which results in problems to recover the aforesaid intermediates and products efficiently from such solvents.

It is, therefore, an object of the present invention to provide a solvent which can be used in both steps of the process leading to 1,2-diacyl-2-(*t*-alkyl)hydrazines, which is environmentally friendly, which provides good selectivity, purities and yields for the aforesaid intermediates and products, which is easily recovered and recycled in the process, which allows facile removal of the product after completion of the reactions leading to it, which does not participate in the reaction process to provide undesirable side products, and which is economical to utilize. In the present invention, it has been unexpectedly found that esters, more particularly aliphatic esters, possess these desirable attributes. Although US 4,985,461 teaches the use of the solvents listed previously, it does not teach or suggest the use of esters with their attendant advantages as solvents in a process to make 1,2-diacyl-2-(*t*-alkyl)hydrazines.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process, employing an ester or a mixture of an ester and water as the solvent, for the preparation at a temperature between about -20° C and about 100° C of pesticidal 1,2-diacyl-2-(*t*-alkyl)hydrazine compounds of the formula



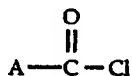
wherein

R¹ is a tertiary (C₄-C₈)alkyl group,

A and B are each independently phenyl, naphthyl, or phenyl or naphthyl

5 substituted with one to three of the same or different substituents selected from the
group consisting of halo, cyano, nitro, hydroxy, mercapto, thiocyanato, (C1-C4)alkyl,
(C1-C4)alkoxy, halo(C1-C2)alkyl, halo(C1-C2)alkoxy, (C1-C4)alkylthio, (C1-
C4)alkylsulfanyl, (C1-C4)alkylsulfonyl, carboxy, formyl, (C1-C4)alkylcarbonyl, (C1-
C4)alkoxycarbonyl, (C1-C4)alkanoyloxy, amino, (C1-C4)alkylamino, di(C1-
10 C4)alkylamino having independently the stated number of carbon atoms in each alkyl
group, carbamoyl, (C1-C4)alkylcarbamoyl, di(C1-C4)alkylcarbamoyl having
independently the stated number of carbon atoms in each alkyl group, cyano(C1-
C4)alkyl, (C1-C4)alkoxy(C1-C4)alkyl, (C2-C6)alkenyl, (C4-C6)alkadienyl, (C2-
C6)alkynyl, (C1-C4)alkyldithionate, (C1-C4)alkylcarbonylthio, tri(C1-C4)alkylsilyl
15 having independently the stated number of carbon atoms in each alkyl group, phenyl,
phenyl substituted with one to two of the same or different substituents selected from
the group consisting of halo, cyano, nitro, hydroxy, (C1-C4)alkyl, (C1-C4)alkoxy,
halo(C1-C2)alkyl, halo(C1-C2)alkoxy, (C1-C4)alkylthio, (C1-C4)alkylsulfanyl, (C1-
C4)alkylsulfonyl, carboxy, formyl, (C1-C4)alkylcarbonyl, (C1-C4)alkoxycarbonyl, (C1-
20 C4)alkanoyloxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino having
independently the stated number of carbon atoms in each alkyl group, phenoxy,
phenoxy substituted with one to two of the same or different substituents selected from
the group consisting of halo, cyano, nitro, hydroxy, (C1-C4)alkyl, (C1-C4)alkoxy,
halo(C1-C2)alkyl, halo(C1-C2)alkoxy, (C1-C4)alkylthio, (C1-C4)alkylsulfanyl, (C1-
25 C4)alkylsulfonyl, carboxy, formyl, (C1-C4)alkylcarbonyl, (C1-C4)alkoxycarbonyl, (C1-
C4)alkanoyloxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino having
independently the stated number of carbon atoms in each alkyl group, benzoyl, benzoyl
substituted with one to two of the same or different substituents selected from the
group consisting of halo, cyano, nitro, hydroxy, (C1-C4)alkyl, (C1-C4)alkoxy, halo(C1-
30 C2)alkyl, halo(C1-C2)alkoxy, (C1-C4)alkylthio, (C1-C4)alkylsulfanyl, (C1-
C4)alkylsulfonyl, carboxy, formyl, (C1-C4)alkylcarbonyl, (C1-C4)alkoxycarbonyl, (C1-
C4)alkanoyloxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino having
independently the stated number of carbon atoms in each alkyl group,
phenoxycarbonyl, phenoxycarbonyl substituted with one to two of the same or different
35 substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C1-
C4)alkyl, (C1-C4)alkoxy, halo(C1-C2)alkyl, halo(C1-C2)alkoxy, (C1-C4)alkylthio, (C1-

- C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenylthio, phenylthio substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenyl(C₁-C₄)alkyl, phenyl(C₁-C₄)alkyl substituted on the phenyl ring with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group; or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano (methylenedioxy) or dioxano (1,2-ethylenedioxy) heterocyclic ring; and the agronomically acceptable salts thereof;
- whereby said process comprises:
- a. reacting an aromatic acid chloride of the formula

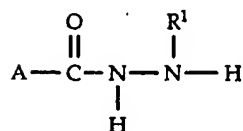


- with a tertiary (C₄-C₈)alkylhydrazine of the formula



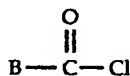
- or a corresponding acid addition salt of said tertiary (C₄-C₈)alkylhydrazine in the presence of a base to form an intermediate 1-acyl-2-(*t*-alkyl)hydrazine of the formula

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wherein A and R¹ have the same definitions as previously; and

- b. reacting said intermediate hydrazine from step a with an aromatic acid
5 chloride of the formula



in the presence of a base to form the said 1,2-diacyl-2-(*t*-alkyl)hydrazine wherein B has
the same definitions as previously.

DETAILED DESCRIPTION OF THE INVENTION

Halo is chloro, fluoro, bromo or iodo.

- (C₁-C₄)alkyl is a straight chain or branched chain alkyl group, for
15 example, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl or *t*-butyl.

Tertiary (C₄-C₈)alkyl is, for example, *t*-butyl, 1,1-dimethylpentyl and
1,1,3,3-tetramethylbutyl.

(C₂-C₆)alkenyl is, for example, vinyl, allyl or 2-buten-1-yl.

(C₄-C₆)alkadienyl is, for example, 2,4-pentadien-1-yl.

- (C₂-C₆)alkynyl is, for example, propargyl.

(C₁-C₄)alkoxy is, for example, methoxy, ethoxy or isopropoxy.

(C₁-C₄)alkoxy(C₁-C₄)alkyl is, for example, methoxymethyl or 2-
methoxyethyl.

- Halo(C₁-C₂)alkyl is, for example, trifluoromethyl, 1,1,2,2,2-
25 pentafluoroethyl or chloromethyl.

Halo(C₁-C₂)alkoxy is, for example, difluoromethoxy.

(C₁-C₄)alkylthio is, for example, methylthio.

(C₁-C₄)alkylcarbonyl is, for example, methylcarbonyl (acetyl).

(C₁-C₄)alkoxycarbonyl is, for example, ethoxycarbonyl.

- (C₁-C₄)alkanoyloxy is, for example, methylcarbonyloxy (acetoxy).

(C₁-C₄)alkylamino is, for example, isobutylamino.

Di(C₁-C₄)alkylamino is, for example, dimethylamino or N-methyl-N-

ethylamino.

(C₁-C₄)alkylcarbamoyl is, for example, *n*-butylcarbamoyl.

Di(C₁-C₄)alkylcarbamoyl is, for example, dimethylcarbamoyl or *N*-methyl-*N*-ethylcarbamoyl.

5 (C₁-C₄)alkylsulfinyl is, for example, methylsulfinyl.

(C₁-C₄)alkylsulfonyl is, for example, methylsulfonyl.

(C₁-C₄)alkyldithionate is, for example, methyl dithionate.

(C₁-C₄)alkylcarbonylthio is, for example, ethylcarbonylthio.

Tri(C₁-C₄)alkylsilyl is, for example, trimethylsilyl or diethylmethylsilyl.

10 Phenyl(C₁-C₄)alkyl is, for example, benzyl or 4-chlorophenethyl.

Methylenedioxy is the -OCH₂O- moiety.

1,2-Ethylenedioxy is the -OCH₂CH₂O- moiety.

Typical acid chlorides which may be used in the process of the present invention include, but are not limited to, benzoyl chloride, 3-methylbenzoyl chloride, 15 3,5-dimethylbenzoyl chloride, 3,5-dichlorobenzoyl chloride, 4-ethylbenzoyl chloride, 4-chlorobenzoyl chloride, 2-methyl-3-methoxybenzoyl chloride, 3,5-dichlorobenzoyl chloride, 3-chlorobenzoyl chloride, 4-cyanobenzoyl chloride, 3-nitrobenzoyl chloride, 2,3-dimethylbenzoyl chloride, 3-methoxybenzoyl chloride, 3-fluorobenzoyl chloride, 4-(*t*-butyl)benzoyl chloride, 2,4-dichlorobenzoyl chloride, 3-(trifluoromethyl)benzoyl 20 chloride, 2-acetoxymethylbenzoyl chloride, 4-(4-chlorophenethyl)benzoyl chloride, 1-naphthoyl chloride, 4-isopropylbenzoyl chloride, 2,6-difluorobenzoyl chloride, 2-(difluoromethoxy)benzoyl chloride, 4-acetylbenzoyl chloride, 3-(dimethylamino)benzoyl chloride, 2-nitro-4-((4-trifluoromethyl)-2-chlorophenoxy)benzoyl chloride, phenylthiobenzoyl chloride, 4-(2-fluorobenzyl)benzoyl chloride, 4-(4-chlorobenzoyl)benzoyl chloride, 4-(phenoxy)benzoyl chloride, 2-methyl-3,4-(1,2-ethylenedioxy)benzoyl chloride, 2-methyl-3,4-(methylenedioxy)benzoyl chloride, and the like.

Typical tertiary alkylhydrazines which may be used in the process of the present invention include, but are not limited to, *t*-butylhydrazine, 1,1- 30 dimethylpentylhydrazine and 1,1,3,3-tetramethylbutylhydrazine and the like and their corresponding acid addition salts such as the hydrochloride salt, for example, *t*-butylhydrazine hydrochloride.

Typical 1,2-diacyl-2-(*t*-alkyl)hydrazine products which may be produced by the process of this invention include, but are not limited to, *N'*-*t*-butyl-*N,N'*- 35 dibenzoylhydrazine, *N'*-*t*-butyl-*N*-(4-chlorobenzoyl)-*N'*-benzoylhydrazine, *N'*-*t*-butyl-*N*-(4-ethylbenzoyl)-*N'*-(3,5-dimethylbenzoyl)hydrazine, *N'*-*t*-butyl-*N*-(2-methyl-3-

methoxybenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-*t*-butyl-N-(4-ethylbenzoyl)-N'-(3-methylbenzoyl)hydrazine, N'-*t*-butyl-N-(2-ethyl-3-methoxybenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-*t*-butyl-N-(2,3-dimethylbenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-*t*-butyl-N-(2,3-dimethylbenzoyl)-N'-(3-methylbenzoyl)hydrazine, N'-*t*-butyl-N-(4-ethylbenzoyl)-N'-(3,5-dichlorobenzoyl)hydrazine, N'-*t*-butyl-N-(2-methyl-3,4-(1,2-ethylenedioxy)benzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-*t*-butyl-N-(2-methyl-3,4-(methylenedioxy)benzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-*t*-butyl-N-(2-fluorobenzoyl)-N'-benzoylhydrazine, N'-*t*-butyl-N-(1-naphthoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, N'-(1,1-dimethylpentyl)-N-(4-chlorobenzoyl)-N'-benzoylhydrazine and N'-(1,1,3,3-tetramethylbutyl)-N-(2-methyl-3-methoxybenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine, and the like.

Typical esters which may be employed as solvents or cosolvents with water in the process of this invention include, but are not limited to, (C₁-C₄)alkyl (C₁-C₅)alkanoates such as *n*-butyl acetate, methyl *n*-butyrate, ethyl isopropionate, *n*-propyl acetate, isopropyl acetate, ethyl acetate, methyl pentanoate, isobutyl acetate, ethyl *n*-butyrate, and the like.

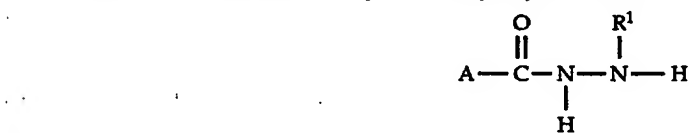
In the process of the present invention, an aromatic acid chloride of the formula



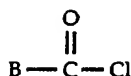
is reacted with a tertiary (C₄-C₈)alkylhydrazine of the formula



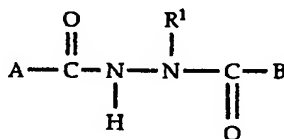
or a corresponding acid addition salt of the tertiary (C₄-C₈)alkylhydrazine in the presence of a base in an ester solvent or a mixture of water and an ester solvent to form an intermediate 1-acyl-2-(*t*-alkyl)hydrazine of the formula



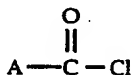
wherein A and R¹ have the same definitions as previously; and then reacting the intermediate hydrazine with an aromatic acid chloride of the formula



- 5 in the presence of a base and the same ester solvent or a mixture of water and the same ester solvent to form the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine product having the formula



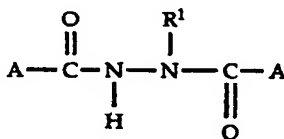
- 10 wherein A, B and R¹ are the same as defined previously. When A and B are the same, for example, both A and B are 4-chlorophenyl, two equivalents of the aromatic acid chloride of the formula



- 15 are reacted with a tertiary (C₄-C₈)alkylhydrazine of the formula



- 20 or a corresponding acid addition salt of the tertiary (C₄-C₈)alkylhydrazine in the presence of a base in an ester solvent or a mixture of water and an ester solvent to form the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine product having the formula



- 25 wherein A and R¹ are the same as defined previously.

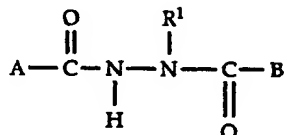
Examples of bases for use in the process of the present invention include, but are not limited to, tertiary amines such as triethylamine, pyridine, potassium carbonate, sodium carbonate, sodium bicarbonate, potassium bicarbonate, sodium hydroxide, potassium hydroxide or mixtures thereof.

The process of the present invention can be carried out at temperatures between about -20° C and about 100° C at about atmospheric pressure, although higher or lower pressures can be used if desired. More specifically, the temperatures utilized in the first step (step a) of the present process are in the range between about -20° C and about 40° C. The temperatures utilized in the second step (step b) of the present process are in the range between about 25° C and about 100° C.

Substantially equimolar amounts of reactants are used in the process although higher or lower amounts can be used if desired. Generally, from about 1.0 to about 1.5 equivalents of base are used per equivalent of the aromatic acid chloride starting material. When an acid addition salt of the tertiary alkylhydrazine is employed, one additional equivalent of base is employed.

Modifications to the process of the present invention may be necessary to accommodate reactive functionalities of particular A and/or B substituents. Such modifications would be apparent and known to those skilled in the art. Procedures for making the agronomically acceptable salts embraced by the products resulting from the process of the present invention are also well known to those skilled in the art and have been previously described.

In a preferred embodiment of the present invention, there is provided a process, employing a (C₂-C₄)alkyl (C₂-C₅)alkanoate ester or a mixture of a (C₂-C₄)alkyl (C₂-C₅)alkanoate ester and water as the solvent, for the preparation of 1,2-diacyl-2-(*t*-alkyl)hydrazine compounds of the formula

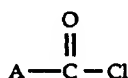


wherein

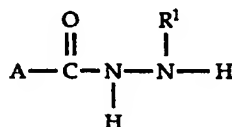
R¹ is *t*-butyl, 1,1-dimethylpentyl or 1,1,3,3-tetramethylbutyl,

A and B are each independently phenyl, naphthyl, or phenyl or naphthyl substituted with one to three of the same or different substituents selected from the group consisting of halo, cyano, nitro, thiocyanato, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, carbamoyl, (C₁-C₄)alkylcarbamoyl, di(C₁-

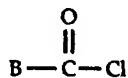
- C₄)alkylcarbamoyl having independently the stated number of carbon atoms in each alkyl group, cyano(C₁-C₄)alkyl, (C₁-C₄)alkoxy(C₁-C₄)alkyl, (C₂-C₆)alkenyl, (C₄-C₆)alkadienyl, (C₂-C₆)alkynyl, (C₁-C₄)alkyldithionate, (C₁-C₄)alkylcarbonylthio, tri(C₁-C₄)alkylsilyl having independently the stated number of carbon atoms in each
- 5 alkyl group, phenyl, phenoxy, benzoyl, phenyl(C₁-C₂)alkyl or phenyl(C₁-C₂)alkyl substituted on the phenyl ring with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, di(C₁-C₄)alkylamino having independently
- 10 the stated number of carbon atoms in each alkyl group; or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano or dioxano heterocyclic ring; and
- the agronomically acceptable salts thereof;
- 15 whereby said process comprises:
- a. reacting an aromatic acid chloride of the formula



- 20 with *t*-butylhydrazine, 1,1-dimethylpentylhydrazine or 1,1,3,3-tetramethylbutylhydrazine or a corresponding acid addition salt of said hydrazine in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate or a mixture thereof at a temperature between about -5° C and about 40° C to form an intermediate 1-acyl-2-(*t*-
- 25 alkyl)hydrazine of the formula

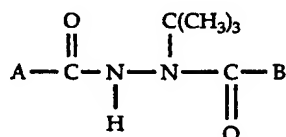


- wherein A and R¹ have the same definitions as previously; and
- 30 b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate or a mixture thereof at a temperature between about 25° C and about 95° C to form the said 1,2-diacyl-2-(*t*-alkyl)hydrazine wherein B has the same definitions as previously.

In a more preferred embodiment of the present invention, there is provided a process, employing a mixture of water and an ester selected from the group consisting of isobutyl acetate, ethyl acetate, isopropyl acetate and *n*-butyl acetate as the solvent, for the preparation of 1,2-diacyl-2-(*t*-butyl)hydrazine compounds of the formula

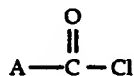


wherein

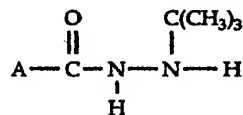
A and B are each independently phenyl, or phenyl substituted with one to three of the same or different substituents selected from the group consisting of halo, (C₁-C₂)alkyl, (C₁-C₂)alkoxy, (C₁-C₂)alkoxy(C₁-C₂)alkyl or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

whereby said process comprises:

a. reacting an aromatic acid chloride of the formula

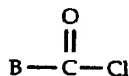


with *t*-butylhydrazine or *t*-butylhydrazine hydrochloride in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, or a mixture thereof to form an intermediate 1-acyl-2-(*t*-butyl)hydrazine of the formula



wherein A has the same definitions as previously; and

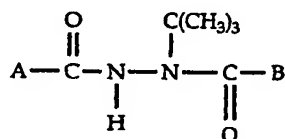
b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



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in the presence of sodium carbonate, sodium bicarbonate or potassium carbonate or a mixture thereof to form the said 1,2-diacyl-2-(*t*-butyl)hydrazine wherein B has the same definitions as previously.

In a most preferred embodiment of the present invention, there is provided a process, employing a mixture of water and *n*-butyl acetate as the solvent, for the preparation of 1,2-diacyl-2-(*t*-butyl)hydrazine compounds of the formula



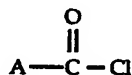
wherein

A is phenyl, 2-fluorophenyl, 4-chlorophenyl, 2-methyl-3-methoxyphenyl or 4-ethylphenyl,

B is phenyl, 3,5-dimethylphenyl, 3-methylphenyl, 3-chlorophenyl or 3,5-dichlorophenyl;

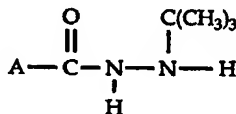
whereby said process comprises:

a. reacting an aromatic acid chloride of the formula



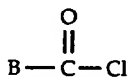
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with *t*-butylhydrazine hydrochloride in the presence of a mixture of sodium hydroxide and potassium carbonate to form an intermediate 1-acyl-2-(*t*-butyl)hydrazine of the formula



wherein A has the same definitions as previously; and

b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



- 5 in the presence of sodium carbonate or potassium carbonate to form the said 1,2-diacyl-2-(*t*-butyl)hydrazine wherein B has the same definitions as previously.

10 The following examples are merely provided to illustrate the process of the present invention. They are not intended to limit the scope of the invention which is defined by the claims.

EXAMPLE 1: PREPARATION OF N'-*t*-BUTYL-N-(4-ETHYLBENZOYL)-N'-(3,5-DIMETHYLBENZOYL)HYDRAZINE

STEP A: To a flask inerted with nitrogen is added 65.4 grams (g) of *t*-butylhydrazine hydrochloride and 50 g of water. The temperature is maintained at 20° C or lower as 78.8 g of 20% sodium hydroxide solution is charged while stirring the flask contents. This is followed by the addition of a solution of 36.2 g of potassium carbonate in 50 g of water. The reaction mixture is cooled to 15° C and 300 g of *n*-butyl acetate is added. While continuing stirring at 15° C, 84.3 g of 4-ethylbenzoyl chloride and 100g of 20% sodium hydroxide solution are cofed to the reaction mixture over a one hour period. The resulting slurry is held an additional 30 minutes at 15° C and is then heated to 40° C. The solids dissolve and the aqueous phase is removed. The *n*-butyl acetate phase is washed with 100 g of water and the wash discarded.

STEP B: To the *n*-butyl acetate phase is added 100 g of water and the resulting mixture is heated to 60° C. An aqueous potassium carbonate solution, which is prepared from 37.3 g of anhydrous potassium carbonate, and 84.3 g of 3,5-dimethylbenzoyl chloride are cofed to the stirred reaction mixture. When the feeds are 50% complete, the reaction mixture is seeded with 0.18 g of N'-*t*-butyl-N-(4-ethylbenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine. After the appearance of solids, the feeds are resumed. After completion of the feeds, the reaction mixture is stirred an additional hour at 60° C and then the phases are allowed to settle. The aqueous phase is discarded and the slurry is washed twice with 100 g portions of water at 60° C and then cooled to 5° C. The solids are filtered, washed with cold *n*-butyl acetate and then dried under vacuum resulting in the recovery of N'-*t*-butyl-N-(4-ethylbenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine as white solid of 96.5% purity.

EXAMPLES 2-5:

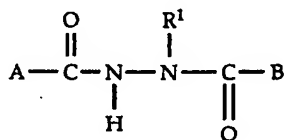
- By following substantially the same procedure as Example 1 and utilizing the aromatic acid chlorides listed for the steps as shown, the following compounds may be prepared as further illustrations of the process of this invention:

EX. NO.	STEP A	STEP B	PRODUCT
2	benzoyl	benzoyl	N'-t-butyl-N,N'-dibenzoylhydrazine
10 3	2-fluorobenzoyl	benzoyl	N'-t-butyl-N-(2-fluorobenzoyl)-N'-benzoylhydrazine
4	4-chlorobenzoyl	benzoyl	N'-t-butyl-N-(4-chlorobenzoyl)-N'-benzoylhydrazine
5	2-methyl-3-methoxybenzoyl	3,5-dimethyl-benzoyl	N'-t-butyl-N-(2-methyl-3-methoxybenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine

- It should be understood that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention as defined by the appended claims.

I CLAIM:

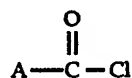
1. A process, employing an ester or a mixture of an ester and water as the solvent, for the preparation of pesticidal 1,2-diacyl-2-(*t*-alkyl)hydrazine compounds of the formula



wherein

- 10 R^1 is a tertiary (C₄-C₈)alkyl group,
 A and B are each independently phenyl, naphthyl, or phenyl or naphthyl substituted with one to three of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, mercapto, thiocyanato, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, carbamoyl, (C₁-C₄)alkylcarbamoyl, di(C₁-C₄)alkylcarbamoyl having independently the stated number of carbon atoms in each alkyl group, cyano(C₁-C₄)alkyl, (C₁-C₄)alkoxy(C₁-C₄)alkyl, (C₂-C₆)alkenyl, (C₄-C₆)alkadienyl, (C₂-C₆)alkynyl, (C₁-C₄)alkyldithionate, (C₁-C₄)alkylcarbonylthio, tri(C₁-C₄)alkylsilyl having independently the stated number of carbon atoms in each alkyl group, phenyl, phenyl substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenoxy, phenoxy substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having

- independently the stated number of carbon atoms in each alkyl group, benzoyl, benzoyl substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenoxycarbonyl, phenoxycarbonyl substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenylthio, phenylthio substituted with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, phenyl(C₁-C₄)alkyl, phenyl(C₁-C₄)alkyl substituted on the phenyl ring with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, amino, (C₁-C₄)alkylamino, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group; or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano (methylenedioxy) or dioxano (1,2-ethylenedioxy) heterocyclic ring; and the agronomically acceptable salts thereof;
- whereby said process comprises:
- reacting an aromatic acid chloride of the formula

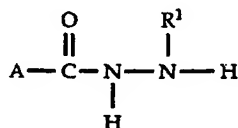


- with a tertiary (C₄-C₈)alkylhydrazine of the formula

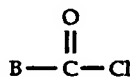
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- 5 or a corresponding acid addition salt of said tertiary (C₄-C₈)alkylhydrazine in the presence of a base, at a temperature between about -20° C and about 40° C, to form an intermediate 1-acyl-2-(*t*-alkyl)hydrazine of the formula

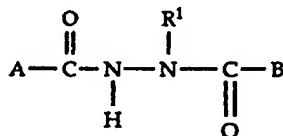


- 10 wherein A and R¹ have the same definitions as previously; and
b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



- 15 in the presence of a base, at a temperature between about 25° C and about 100° C, to form the said 1,2-diacyl-2-(*t*-alkyl)hydrazine wherein B has the same definitions as previously.

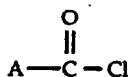
2. The process of claim 1, employing a (C₂-C₄)alkyl (C₂-C₅)alkanoate ester
20 or a mixture of a (C₂-C₄)alkyl (C₂-C₅)alkanoate ester and water as the solvent, for the preparation of 1,2-diacyl-2-(*t*-alkyl)hydrazine compounds of the formula



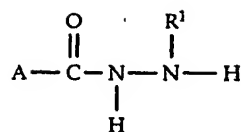
- 25 wherein

- R¹ is *t*-butyl, 1,1-dimethylpentyl or 1,1,3,3-tetramethylbutyl,
A and B are each independently phenyl, naphthyl, or phenyl or naphthyl
substituted with one to three of the same or different substituents selected from the
group consisting of halo, cyano, nitro, thiocyanato, (C₁-C₄)alkyl, (C₁-C₄)alkoxy,
30 halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-

- C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group, carbamoyl, (C₁-C₄)alkylcarbamoyl, di(C₁-C₄)alkylcarbamoyl having independently the stated number of carbon atoms in each alkyl group, cyano(C₁-C₄)alkyl, (C₁-C₄)alkoxy(C₁-C₄)alkyl, (C₂-C₆)alkenyl, (C₄-C₆)alkadienyl, (C₂-C₆)alkynyl, (C₁-C₄)alkyldithionate, (C₁-C₄)alkylcarbonylthio, tri(C₁-C₄)alkylsilyl having independently the stated number of carbon atoms in each alkyl group, phenyl, phenoxy, benzoyl, phenyl(C₁-C₂)alkyl or phenyl(C₁-C₂)alkyl substituted on the phenyl ring with one to two of the same or different substituents selected from the group consisting of halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo(C₁-C₂)alkyl, halo(C₁-C₂)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, carboxy, formyl, (C₁-C₄)alkylcarbonyl, (C₁-C₄)alkoxycarbonyl, (C₁-C₄)alkanoyloxy, di(C₁-C₄)alkylamino having independently the stated number of carbon atoms in each alkyl group; or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano or dioxano heterocyclic ring; and the agronomically acceptable salts thereof; whereby said process comprises:
- a. reacting an aromatic acid chloride of the formula

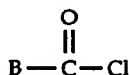


- with *t*-butylhydrazine, 1,1-dimethylpentylhydrazine or 1,1,3,3-tetramethylbutylhydrazine or a corresponding acid addition salt of said hydrazine in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate or a mixture thereof at a temperature between about -5° C and about 40° C to form an intermediate 1-acyl-2-(*t*-alkyl)hydrazine of the formula



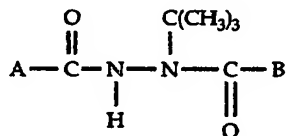
wherein A and R¹ have the same definitions as previously; and

- 5 b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



- 10 in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate or a mixture thereof at a temperature between about 25° C and about 95° C to form the said 1,2-diacyl-2-(*t*-alkyl)hydrazine wherein B has the same definitions as previously.

3. The process according to claim 2, employing a mixture of water and an ester selected from the group consisting of isobutyl acetate, ethyl acetate, isopropyl acetate and *n*-butyl acetate as the solvent, for the preparation of 1,2-diacyl-2-(*t*-butyl)hydrazine compounds of the formula

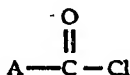


wherein

- 20 A and B are each independently phenyl, or phenyl substituted with one to three of the same or different substituents selected from the group consisting of halo, (C₁-C₂)alkyl, (C₁-C₂)alkoxy, (C₁-C₂)alkoxy(C₁-C₂)alkyl or when two adjacent positions on a phenyl ring are substituted with alkoxy groups, these groups may be joined to form a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

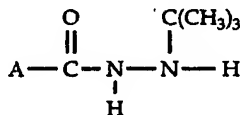
- 25 whereby said process comprises:

- a. reacting an aromatic acid chloride of the formula



with *t*-butylhydrazine or *t*-butylhydrazine hydrochloride in the presence of potassium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, or a mixture thereof to form an intermediate 1-acyl-2-(*t*-butyl)hydrazine of the formula

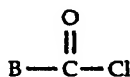
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wherein A has the same definitions as previously; and

- b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula

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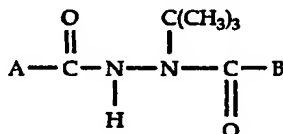


- in the presence of sodium carbonate, sodium bicarbonate potassium carbonate or a mixture thereof to form the said 1,2-diacyl-2-(*t*-butyl)hydrazine wherein B has the same definitions as previously.

15

4. The process according to claim 3, employing a mixture of water and *n*-butyl acetate as the solvent, for the preparation of 1,2-diacyl-2-(*t*-butyl)hydrazine compounds of the formula

20



wherein

A is phenyl, 2-fluorophenyl, 4-chlorophenyl, 2-methyl-3-methoxyphenyl or 4-ethylphenyl,

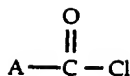
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B is phenyl, 3,5-dimethylphenyl, 3-methylphenyl, 3-chlorophenyl or 3,5-dichlorophenyl;

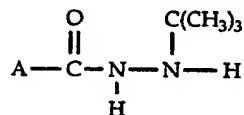
whereby said process comprises:

- a. reacting an aromatic acid chloride of the formula

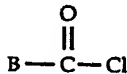
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5 with *t*-butylhydrazine hydrochloride in the presence of a mixture of sodium hydroxide and potassium carbonate to form an intermediate 1-acyl-2-(*t*-butyl)hydrazine of the formula



10 wherein A has the same definitions as previously; and
b. reacting said intermediate hydrazine from step a with an aromatic acid chloride of the formula



15 in the presence of sodium carbonate or potassium carbonate to form the said 1,2-diacyl-2-(*t*-butyl)hydrazine wherein B has the same definitions as previously.

5. A pesticidal product selected from the group consisting of
N'-*t*-butyl-N,N'-dibenzoylhydrazine,
N'-*t*-butyl-N-(2-methyl-3-methoxybenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine,
N'-*t*-butyl-N-(4-ethylbenzoyl)-N'-(3,5-dimethylbenzoyl)hydrazine and
20 N'-*t*-butyl-N-(4-chlorobenzoyl)-N'-benzoylhydrazine
which are produced in accordance with the process of claim 1.

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